SHOCK-TUBE AND MODELING STUDY OF SOOT FORMATION IN MIXTURES OF HYDROCARBONS

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INTRODUCTION

Interest in soot formation in binary hydrocarbon mixtures has increased in recent years. Besides the very practical aspects of such knowledge, the subject is of interest from a fundamental point of view: to provide additional information for the elucidation of the soot formation mechanism. There is evidence, both experimental [1–8] and theoretical [9–11], that the key chemical reactions leading to soot formation in hydrocarbon systems are those between aliphatic and aromatic species. The importance of such reactions was suggested as early as 1960 by Stehling *et al.* [12].

This paper presents the results of a shock-tube pyrolysis study on soot formation from a series of binary hydrocarbon mixtures: benzene–additive, where the additives were acetylene, allene, vinylacetylene and 1,3–butadiene; and allene–acetylene, butadiene–acetylene and acetylene–hydrogen.

EXPERIMENTAL

The experiments were conducted behind reflected shock waves in a 7.62 cm i.d. shock tube [4–6]. Ten different mixtures were tested during the course of this study. The experimental conditions which were chosen such as to allow comparison with the previous results [5,6]. The experiments were carried out at temperatures from 1500 K to 2490 K, pressures from 1.3 to 3.1 bar, and carbon atom concentrations from 2.0 to 6.8×10^{17} atoms/cm^3. The appearance of soot was monitored by the attenuation of a He–Ne laser beam (632.8 nm) at approximately 10 mm from the end plate of the shock tube. The term soot has been used in our work as a lumped property meaning "species absorbing at a 632.8 nm". For its practical measure, the amount of carbon atoms accumulated in soot is used in this work. The latter property is calculated following the usual Raylegh approximation [13] using the complex refractive index of Dalzell and Sarofim [14].

The experimental results are presented for a reaction time of 1 ms; this time is chosen arbitrary — qualitatively similar results were obtained at all observation times.

RESULTS AND DISCUSSION

Acetylene–Hydrogen

Figure 1 depicts the comparison of soot carbon obtained in a acetylene–hydrogen mixture with those obtained at similar conditions from acetylene alone. As can be seen in this figure, hydrogen strongly suppresses soot formation from acetylene. Wang et al. [15] also observed the suppression effect of hydrogen in toluene–hydrogen mixtures. A chemical kinetic model [9,10] predicts this effect: addition of molecular hydrogen increases the reverse rate of the "reactivation", H–atom abstraction reactions.

Allene–Acetylene and Butadiene–Acetylene

Figures 2 and 3 present the amount of soot formed in mixtures of acetylene with allene and 1,3–butadiene, respectively, and a comparison with the results for the individual fuels. A pronounced synergistic effect is observed for these cases.

A computer simulation for the conditions of a butadiene–acetylene mixture with a mechanism of butadiene pyrolysis [10] qualitatively predicts the experimentally observed synergistic effect (the lack of quantitative agreement, as discussed previously [10,16], is due to insufficient knowledge of thermochemical data). The results of the computer simulation are given in Fig. 4. The analysis of the computational results revealed that the main factor affecting soot formation is the increase in the rate of acetylene–addition reactions. This accelerates cyclization reactions and suppresses decomposition of $n-C_xH_y$ radicals to C_2H_2 and $n-C_{x-2}H_{y-2}$. The reaction pathway to soot is similar to that identified for pyrolysis of butadiene [10], except that cyclization via

$$n-C_4H_5 + C_2H_2 \longrightarrow n-C_6H_7$$
$$n-C_6H_7 \longrightarrow c-C_6H_7$$
$$c-C_6H_7 \longrightarrow \text{benzene} + H,$$

becomes more prominent (yet still slower than the reaction sequence via $n-C_6H_5$ [9],

$$n-C_4H_3 + C_2H_2 \longrightarrow n-C_6H_5$$
$$n-C_6H_5 \longrightarrow \text{phenyl},$$

at the conditions of the soot yield maximum).

Based on the computational analysis of the butadiene–acetylene case, the experimental results obtained for allene–acetylene mixtures (Fig. 2) may indicate the importance of sequential addition of two acetylene molecules to $CH_2{=}C{=}CH\bullet$ radical followed by cyclization to a relatively stable benzyl radical. In other words, we propose that in an allene system the first–ring cyclization is not the formation of phenyl or benzene but rather that of benzyl.

Benzene–Additives

Figures 5 and 6 present the results obtained in mixtures of benzene with aliphatic hydrocarbons. Addition of acetylene (Fig. 5) enhances soot formation. However, the effect is pronounced only at relatively high (2.72 and 1.09 %) initial concentration of acetylene. With smaller amounts (0.54 %) of acetylene added, there is no significant increase in soot production; on the contrary, there is a slight suppression of soot formation at lower temperatures.

The main feature of the dominant reaction pathway to soot identified for benzene pyrolysis [10] is the formation of byphenyl by the addition of phenyl radical to benzene followed by sequential addition of two acetylene molecules to form pyrene. The initial presence of acetylene, as revealed by the results of a computer simulation using a benzene pyrolysis mechanism [10], increases the rate of the ring–growth process and suppresses the rate of phenyl fragmentation, both being promoting factors. However, reaction of acetylene with phenyl forming phenylacetylene removes phenyl radicals from a more efficient ring–forming pathway, addition to benzene molecules, which counteracts the promoting factors.

The experimental results reported in Fig. 6 show that vinylacetylene and 1,3–butadiene are more efficient soot promoters than acetylene. Soot–yield maxima in their mixtures with benzene are shifted to higher temperatures compared to that of benzene alone, which indicates that decomposition of the additives is important. The results of computer simulations, which reproduced (again, qualitatively) the experimental trends, support this conclusion. For instance, in the benzene–vinylacetylene case, decomposition of vinylacetylene via

$$C_4H_4 \longrightarrow C_4H_3 + H$$

initiates the pyrolysis. Reactions of C_4H_4, C_4H_3 and C_2H_3 enhance the growth of aromatics compared to the pyrolysis of benzene alone. For example, reaction sequence

$$\begin{aligned} Ph + C_4H_4 &\longrightarrow PhCHCHCCH + H \\ PhH + n\text{–}C_4H_3 &\longrightarrow PhCHCHCCH + H \\ PhCHCHCCH + H &\longrightarrow \bullet PhCHCHCCH + H_2 \\ \bullet PhCHCHCCH &\longrightarrow 2\text{–naphthyl}, \end{aligned}$$

where •PhCHCHCCH is an *ortho*–substituted phenyl radical, is accelerated with the addition of vinylacetylene to benzene.

The results obtained in a benzene–allene mixture (Fig. 4) indicate a synergistic effect. Thus, not only does allene have a high sooting tendency itself [6], but it appears to be also an efficient soot promoter.

ACKNOWLEDGEMENT

The work was supported by Aerochemistry Branch of NASA–Lewis Research Center, Grants Nos. NAG 3–477 and NAG 3–668.

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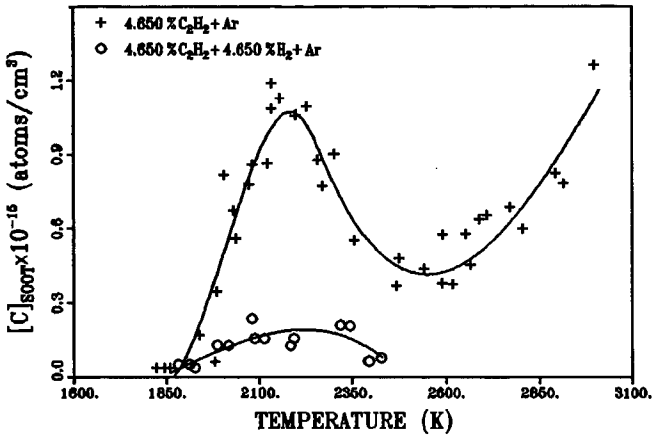

Figure 1. Comparison of soot carbon in pyrolysis of acetylene and acetylene-hydrogen mixture.

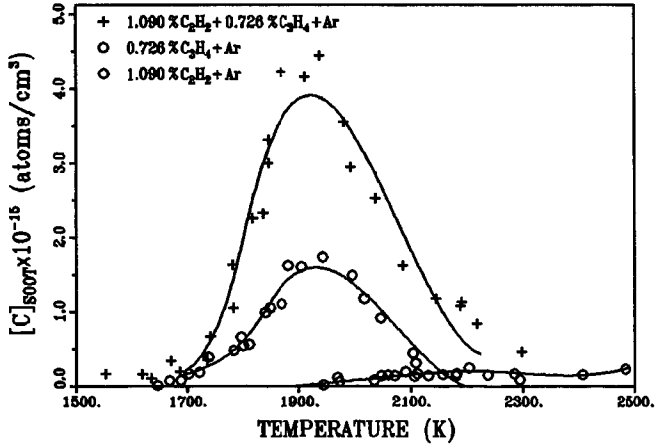

Figure 2. Comparison of soot carbon in pyrolysis of acetylene, allene, and acetylene-allene mixture.

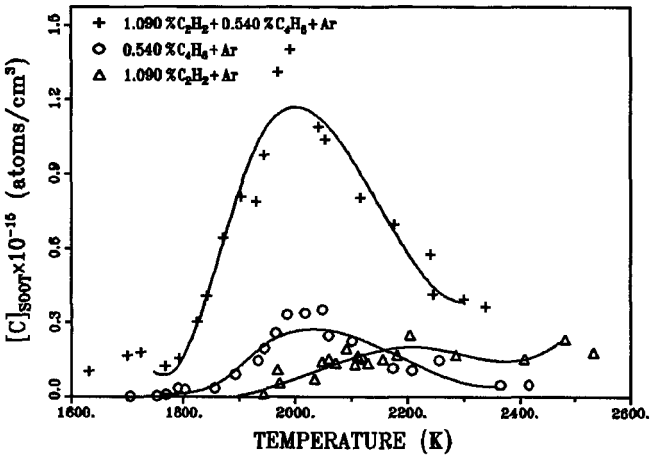

Figure 3. Comparison of soot carbon in pyrolysis of acetylene, 1,3-butadiene, and acetylene-butadiene mixture.

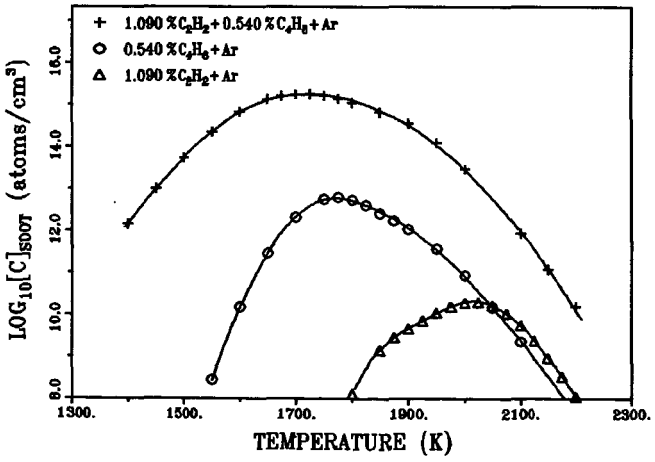

Figure 4. Comparison of computed soot carbon in pyrolysis of acetylene, 1,3-butadiene, and acetylene-butadiene mixture.

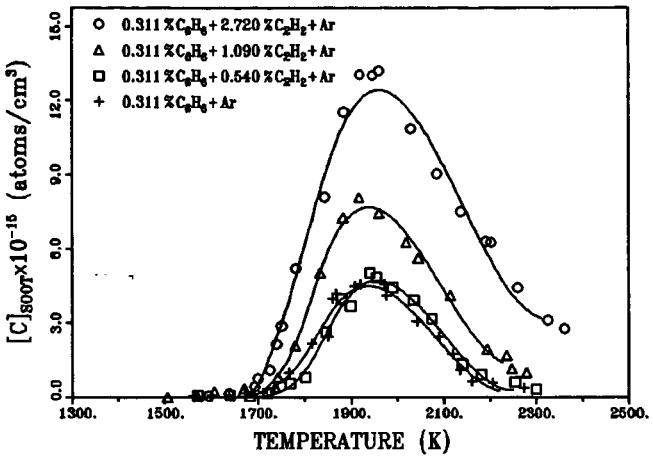

Figure 5. Comparison of soot carbon in pyrolysis of benzene, and benzene-acetylene mixture.

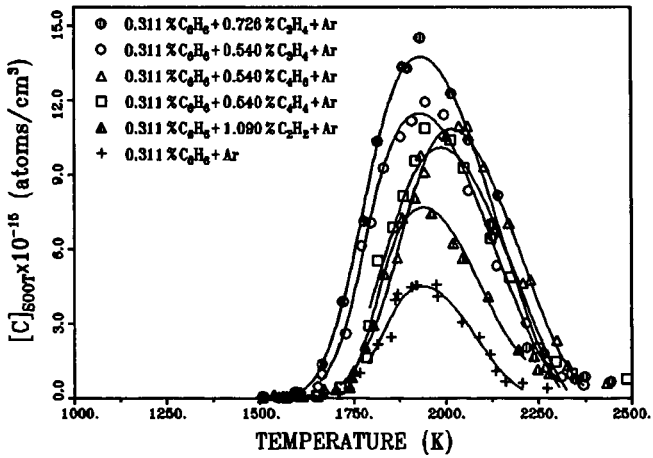

Figure 6. Comparison of soot carbon in pyrolysis of benzene, benzene-acetylene, benzene-allene, benzene-vinylacetylene, and benzene-butadiene mixtures.